

The University of Chicago

I. THE ADDITION OF NITROSYL
HALIDES TO ISOBUTYLENE
II. CLEAVAGE OF *aaa*-TRICHLORO-
ACETOPHENONES

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1936

By

WALLACE ALFRED ERICKSON

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The author wishes to express his
sincere appreciation to Professor
M. S. Kharasch, who directed this work.

PART I

THE ADDITION OF NITROSYL HALIDES TO ISOBUTYLENE

It has been demonstrated in this laboratory that the addition of some reagents to olefinic double bonds is governed by heretofore unknown factors. A case in point is the addition of the hydrogen halides to isobutylene.¹

It was here found that pure hydrogen bromide reacted with pure isobutylene to yield tertiary butyl bromide. However, if 0.03 to 0.04 mol of ascaridole (an organic peroxide) per mol of isobutylene were present the reaction yielded at least 80% isobutylbromide. Under these same conditions hydrogen chloride reacted with isobutylene to form only tertiary butyl chloride.²

The present study of the addition of nitrosyl halides to isobutylene was undertaken to determine whether these would behave in a manner similar to the hydrogen halides.

Results.--Pure nitrosyl chloride was found to react with pure isobutylene to form the oxime of α -chlorisobutyraldehyde. In the presence of 5% by weight of ascaridole the identical product was formed.

No reference could be found in the literature to the addition of nitrosyl bromide to any unsaturated compounds, although the literature concerning nitrosyl chloride in such reactions is abundant. When nitrosyl bromide was reacted with isobutylene, in a manner similar to that used for the addition of nitrosyl chloride, nitric oxide gas was evolved and isobutylene dibromide was formed in the reaction tube. The identical reaction occurred in the presence of 5% of ascaridole.

Experimental Part

Isobutylene.--This material was prepared according to the

¹M. S. Kharasch and John A. Hinckley, Jr., J. Am. Chem. Soc., 56, 1243 (1934).

²M. S. Kharasch and John A. Hinckley, Jr., unpublished work.

direction of Hurd and Spence.¹ Two hundred cc. of tertiary butyl alcohol was refluxed with 75 grams of ordinary commercial oxalic acid. The gases which escaped from the top of the condenser were led into and condensed in a tube surrounded by a bath of carbon dioxide snow and acetone. The product, distilled twice from calcium chloride, weighed 110 grams.

Nitrosyl chloride.--This material was most conveniently prepared by the method of Whittaker, Lundstrom and Merz.² Five hundred grams of potassium chloride was moistened with 12 cc. (2.4%) of water and the mixture let stand for twenty-four hours to distribute the water uniformly. The salt was then placed in a vertical, wide glass tube, one meter in length, fitted with a 250 cc. flask at the lower end. One hundred and seventy-six grams of nitrogen tetroxide was placed in the flask and the flask surrounded by a bath of warm water. This caused the vapors of nitrogen dioxide to be forced upwards through the tube of potassium chloride. The reaction zone could be followed readily as it rose up the tube by the difference in color between the nitrogen dioxide and the nitrosyl chloride. The reaction proceeds according to the equation:



The reaction was stopped when about 10 cc. of potassium chloride remained unreacted at the top of the tube, to assure freedom from oxides of nitrogen in the final product. The nitrosyl chloride was led from the top of the reaction tube into a tube surrounded by a mixture of solid carbon dioxide and acetone, where it condensed and solidified. The product was dried by distillation through a tube packed with fused calcium chloride. The yield of nitrosyl chloride at this point was 100 grams. The product was purified by fractionation through an improvised Davis column.³ Although the entire 100 grams distilled sharply at -5.5° only the middle 75 grams was retained. The deflegmator was

¹Charles D. Hurd and L. V. Spence, J. Am. Chem. Soc., **51**, 3562 (1929).

²Colin W. Whittaker, Frank O. Lundstrom, and Albert R. Merz, Ind. & Eng. Chem., **23**, 1410 (1931).

³Harold S. Davis, Ind. & Eng. Chem., Analytical Edition, **1**, 61 (1929).

kept at -15° to -20° during the distillation. The product froze to a bright orange colored solid at the temperature of carbon dioxide and acetone.

Addition of nitrosyl chloride to isobutylene without added reagents.--Five and six-tenths Grams (.1 mol) of isobutylene was placed in a tube surrounded by an ice and salt mixture at a temperature of -21° . Six and five-tenths Grams (.1 mol) of nitrosyl chloride was slowly passed to the isobutylene whereupon the addition took place smoothly. The tube and contents were permitted to stand over night to attain room temperature slowly. The reactants, being volatile, were thus removed leaving 8.8 grams of solid product in the tube. After two crystallizations from ligroin, 5.4 grams of pure product were obtained, m. p., $103-104^{\circ}$. This corresponds to the product previously described in the literature formed by the action of concentrated hydrochloric acid and amyl nitrite on isobutylene.^{1,2,3}

The above experiment was repeated using 11.2 grams (0.2 mol) of isobutylene and 6.5 grams (0.1 mol) of nitrosyl chloride. After two crystallizations from ligroin, 6.4 grams of pure product was obtained, m. p., 101° .

Addition of nitrosyl chloride to isobutylene in the presence of ascaridole.--In 5.6 grams (0.1 mol) of isobutylene was dissolved 0.3 grams of ascaridole, about 5% by weight (care was taken that solution took place completely). This solution was kept in an ice and salt mixture at -21° while 6.5 grams (0.1 mol) of nitrosyl chloride was slowly passed in. The reaction tube and contents were permitted to warm slowly to room temperature thus removing the volatile reactants. The solid product remaining in the tube weighed 11.7 grams. Two crystallizations from ligroin yielded 5.1 grams of product, m. p., $100-101^{\circ}$.

This experiment was repeated using 11.2 grams (0.2 mol) of isobutylene with 0.6 grams of ascaridole and 6.5 grams (0.1 mol) of nitrosyl chloride. Two crystallizations from ligroin gave 5.7 grams of product, m. p., 100° . An intimate of this material with

¹W. Ipatiew and A. Ssolonina, J. Russ. Phys. Chem. Soc., 33, 496 (1901). Chemisches Central-Blatt, 1901, II, 1201.

²Walter Huckel and Paul Ackermann, J. prakt. Chem., N.F., 136, 25 (1933).

³H. D. K. Drew and F.S.H.Head, J. Chem. Soc., 1934, 49.

the product obtained from the addition of nitrosyl chloride to isobutylene without added reagents of m. p., $103-104^{\circ}$, melted from $100-101^{\circ}$. Therefore the two products are considered to be identical.

Nitrosyl bromide.--The simplest preparation of nitrosyl bromide appeared to be that given by Friend.¹ Nitrosyl sulfuric acid was prepared by saturating concentrated sulfuric acid with the gases (dried over calcium chloride) evolved from a warm mixture of one volume of concentrated nitric acid and four volumes of concentrated hydrochloric acid. Fourteen hundred cc. of nitric acid and 5600 cc. of hydrochloric acid were required to make one liter of concentrated nitrosyl sulfuric acid.

The nitrosyl bromide was prepared by dropping the nitrosyl sulfuric acid on dry sodium bromide and collecting the gases, which were evolved, in a trap submerged in solid carbon dioxide and acetone. The nitrosyl bromide was then distilled from the trap directly into the reaction vessel.

Nitrosyl bromide boils at -2° with dissociation into bromine and nitric oxide.

Addition of nitrosyl bromide to isobutylene without added reagents.--Isobutylene (16.8 grams, 0.3 mol) was distilled into a tube submerged in liquid ammonia (about -34°) and 23 grams (0.2 mol) of nitrosyl bromide passed in.

After twenty hours the dark color was discharged indicating that the addition was complete. After pumping off the excess isobutylene there remained 23 grams of product.

The product was fractionated as follows:

¹John Newton Friend, "A Textbook of Inorganic Chemistry," Vol. VI, Part I, pp. 118-120. J. B. Lippincott & Co., Philadelphia, (1928).

First Distillation

Second Distillation

cc.	Temperature	cc.	Temperature
1st drop	129.0°	1	143.0°
1	140.0°	2	cut 143.0°
2	cut 142.0°	2½	144.0°
3	143.0°	3	145.0°
4	145.0°	3½	146.0°
5	146.5°	4	147.3°
6	147.0°	4½	147.5°
7	148.5°	5	148.0°
8	150.0°	5½	150.0°
9	151.0°	6	151.5°
10	cut 153.5°	6½	cut 153.0°
11	161.0	7	156.0

The recorded boiling point for isobutylene dibromide is: 149.0°.

Anal.: Calc'd for $C_4H_8Br_2$. C, 22.2%; H, 3.7%; Br, 74.1%

Found: C, 24.65%; H, 4.07%; Br, 69.22%
69.27%

Addition of nitrosyl bromide to isobutylene in the presence of ascaridole.--Eighty-four one-hundreths (5% by weight) of ascaridole was carefully dissolved in 16.8 grams (0.3 mol) of isobutylene. This solution was then cooled to the temperature of liquid ammonia and 20.7 grams (0.188 mol) of nitrosyl bromide passed in. In the previous experiments it was observed that a gas was evolved during the addition which turned brown on striking the air. Due to the possibility of the nitrosyl bromide decomposing to give as products of the addition isobutylene dibromide and nitric oxide, it was decided to collect the gases escaping from the reaction tube. This was attempted by connecting an azotometer filled with water to the reaction tube and measuring the volume of the escaping gases. Although only 0.188 mols of nitrosyl bromide was used, 0.341 mols of gas was collected. Obviously some isobutylene and nitrosyl bromide also came over into the azotometer,

as the yield of product was only 21.5 grams (0.1 mol as isobutylene dibromide). However, since the gases were colorless in the azotometer and formed a brown cloud when released into the air, the experiment showed that large quantities of nitric oxide were formed in the reaction.

The product was fractionated as follows:

First Distillation

Second Distillation

cc.	Temperature	cc.	Temperature
1st drop	cut <u>91.0°</u>	1	134.0°
1	127.0°	2	139.5°
2	137.0°	3	cut
3	140.0°	4	<u>145.0°</u>
4	143.0°	4½	146.3°
5	146.0°	5	148.0°
6	147.0°	5½	149.6°
7	149.0°	6	152.0°
8	150.0°	6½	cut <u>154.0°</u>
B½	150.0°	7	159.0°

Anal.: Calc'd for $C_4H_8Br_2$, Br, 74.1%

Found: 69.75%; 69.96%.

Summary

1. Nitrosyl chloride reacts with isobutylene to form chlorisobutyraldehyde oxime.
2. Nitrosyl chloride reacts with isobutylene in the presence of ascaridole to form chlorisobutyraldehyde oxime.
3. Nitrosyl bromide reacts with isobutylene to form isobutylene dibromide and nitric oxide.
4. Nitrosyl bromide reacts with isobutylene in the presence of ascaridole to form isobutylene dibromide and nitric oxide.

PART II

CLEAVAGE OF *aaa*-TRICHLOROACETOPHENONES

Introduction.--In a series of papers of recent date Fuson and co-workers¹ have recorded the results of their work on the preparation and cleavage of *aaa*-trichloracetophenones by aqueous caustic. The compounds studied by these workers were chiefly ortho substituted and were found to be cleaved by aqueous caustic with great difficulty. The conclusion drawn was that the steric influence of the groups orthos to the trichloracetyl group prevented the cleavage from taking place. However, diortho substituted *aaa*-trichloracetophenones containing groups (as carboxyl) which confer caustic solubility to the compound have been prepared and have been found to be readily cleaved by aqueous caustic. Thus it appears that in a study of the effect of ortho substituents on the cleavage reaction of these compounds, the solubility factor must be eliminated. Hence a study of the rates of cleavage of *aaa*-trichloracetophenones, diortho substituted with various types of groups, was undertaken, eliminating the effect of solubility. It was hoped that a relation could be found between the type of the substituent and the reaction rate.

Plan of attack.--A number of *aaa*-trichloracetophenones would be prepared with varied ortho substituents on the benzene nucleus, as methyl, chlor, or nitro groups.

The reaction would be run in a medium which would dissolve completely the alkali and the ketones. For this purpose methanol was chosen although acetone probably would have been a better choice. A known quantity of *aaa*-trichloracetophenone would be dissolved in definite amount of methanol containing a known amount of alkali. Then at definite intervals, samples would be withdrawn and the amount of alkali remaining determined. This would indicate

¹Reynold C. Fuson and co-workers, *J. Am. Chem. Soc.*, 52, 3269 (1930); 53, 3494 (1931); 54, 1114 (1932); 54, 4380 (1932); 55, 3424 (1933); 56, 736 (1934); 56, 1417 (1934).

the extent of the reaction:



However, there are two other reactions which might lead to neutralization of the alkali. The chloroform formed in the above reaction, or the uncleaved trichloroacetone might be attacked by the alkali yielding HCl and acidic organic residue. The extent of these reactions would be determined by analyzing the periodic samples for chloride ions. Further running an identical experiment with chloroform would serve to show directly the effect of alcoholic alkali on chloroform under the conditions of the experiment.

Procedure.--The following compounds were prepared for study; *aaa*-trichloroacetophenone, *aaa*-trichloro-*m*-nitro-acetophenone, *aaa*-trichloro-2, 4, 6-trichloroacetophenone, and *aaa*-trichloro-2, 4, 6-trimethylacetophenone. Two sets of cleavage experiments were run on these compounds, and in each the following procedure was used.

The ketone or chloroform (0.001 mol) was accurately weighed out and transferred to a 500 cc. volumetric flask. Methanol was added to dissolve the reactant, and, when solution was complete the desired amount (0.001 or 0.01 mol) of potassium hydroxide was added in the form of standardized methanol solution. The flask was then filled to the 500 cc. graduation with methanol and the contents of the flask thoroughly mixed. Fifty cc. of solution was pipetted into each of ten tubes, fitted with rubber stoppers, and the tubes placed immediately in a thermostat at 60°. At definite time intervals a tube was removed from the thermostat, the contents placed in a flask and after dilution with water titrated with aqueous nitric acid (standardized against the standard methanol potassium hydroxide solution) to a colorless end-point with phenolphthalein as the indicator. This titre gave the amount of alkali still remaining in the solution at the time the tube was removed from the thermostat.

A chloride determination was then made directly by titration with standardized silver nitrate solution, using potassium chromate as the indicator, after the method of Mohr.

Results.--The data obtained are tabulated below. The graphic representations of these data follow.

Chloroform

0.001 mol chloroform + 0.001 mol KOH

Time	cc. HNO ₃	Mols HNO ₃	Mols Alkali Neutralized	cc. AgNO ₃ 0.0986N	Mols Chlor- ide	Mols Alk Mols Chloride
5 min.	18.78	0.000944	0.000056			
30 min.	18.60	0.000936	0.000064	0.15	0.0000148	4.32
1 hr.	18.10	0.000910	0.000080	0.40	0.0000394	2.03
2 hr.	17.37	0.000874	0.000126	0.80	0.0000789	1.60
6 hr.	14.56	0.000732	0.000268	2.10	0.000207	1.29
10 hr.	12.55	0.000632	0.000368	3.20	0.000316	1.16
14 hr.	10.68	0.000538	0.000462	4.20	0.000414	1.12
18 hr.	9.51	0.000478	0.000522	4.77	0.000470	1.11
29 hr.	6.42	0.000323	0.000677	6.27	0.000618	1.10

aaa-Trichloracetophenone

0.001 Mol Ketone + 0.001 Mol KOH

Time	cc. HNO ₃	Mols HNO ₃	Mols Alkali Neutralized	cc. AgNO ₃ 0.0986N	Mols Chlor- ide	Mols Alk Mols Chloride
5 min.	17.42	0.000876	0.000124	0.65	0.0000641	1.93
1 hr.	16.28	0.000819	0.000181	1.20	0.000118	1.53
2 hr.	15.80	0.000795	0.000205	1.60	0.000158	1.30
6 hr.	13.51	0.000680	0.000320	2.68	0.000264	1.21
10 hr.	11.24	0.000566	0.000434	3.65	0.000360	1.21
14 hr.	9.96	0.000501	0.000499	4.30	0.000424	1.18
18 hr.	8.24	0.000415	0.000585	5.10	0.000503	1.16
24 hr.	9.35	0.000470	0.000530	5.85	0.000577	0.92

aaa-Trichlor-2,4,6-trichloracetophenone

0.001 Mol Ketone + 0.001 Mol KOH

Time	cc. HNO ₃	Mols HNO ₃	Mols Alkali Neutralized	cc. AgNO ₃ 0.0986N	Mols Chlor- ide	Mols Alk. Mols Chloride
5 min.	18.72	0.000942	0.000058	0.15	0.0000148	3.92
1 hr.	17.83	0.000897	0.000103	0.44	0.0000434	2.37
2 hr.	17.21	0.000866	0.000134	0.82	0.0000808	1.66
10 hr.	12.50	0.000629	0.000371	3.12	0.000318	1.17
14 hr.	10.95	0.000551	0.000449	3.96	0.000391	1.15
18 hr.	9.28	0.000467	0.000533	4.80	0.000473	1.13
24 hr.	7.50	0.000377	0.000623	5.55	0.000547	1.14

aaa-Trichlor-m-nitroacetophenone

0.001 Mol Ketone + 0.001 Mol KOH

Time	cc. HNO ₃	Mols HNO ₃	Mols Alkali Neutralized	cc. AgNO ₃ 0.0872N	Mols Chlor- ide	Mols Alk. Mols Chloride
5 min.	15.48	0.000779	0.000221	0.22	0.0000192	11.5
1 hr.	13.47	0.000678	0.000322	0.68	0.0000593	4.43
2 hr.	12.32	0.000620	0.000380	1.17	0.000102	3.73
6 hr.	9.73	0.000489	0.000511	2.17	0.000189	2.70
10 hr.	7.02	0.000356	0.000644	2.92	0.000255	2.53
14 hr.	5.16	0.000259	0.000741	3.48	0.000307	2.41
18 hr.	3.87	0.000195	0.000805	3.94	0.000347	2.32

aaa-Trichlor-2,4,6-trimethylacetophenone

0.001 Mol Ketone + 0.001 Mol KOH

Time	cc. HNO ₃	Mols HNO ₃	Mols Alkali Neutralized	cc. AgNO ₃ 0.0986N	Mols Chlor- ide	Mols Alk. Mols Chlor- ide
5 min.	18.53	0.000932	0.000068			
1 hr.	18.60	0.000936	0.000064	0.30	0.0000296	2.16
2 hr.	18.10	0.000910	0.000090	0.45	0.0000444	2.03
6 hr.	15.52	0.000781	0.000219	1.51	0.000149	1.47
15 hr.	10.90	0.000548	0.000452	3.73	0.000369	1.22
18 hr.	9.85	0.000495	0.000505	4.25	0.000419	1.20
24 hr.	7.70	0.000387	0.000613	5.18	0.000511	1.20

Chloroform

0.001 Mol Chloroform + 0.01 Mol KOH

Time	cc. HNO ₃	Mols HNO ₃	Mols Alkali Neutralized	cc. AgNO ₃ 0.0986N	Mols Chlor- ide	Mols Alk. Mols Chlor- ide
5 min.	41.25	0.00990	0.00010	0.45	0.0000444	2.25
15 min.	40.83	0.00980	0.00020	1.36	0.000134	1.49
30 min.	40.19	0.00964	0.00036	2.58	0.000254	1.42
1 hr.	38.98	0.00936	0.00064	4.95	0.000488	1.31
2 hr.	36.88	0.00885	0.00115	8.92	0.000880	1.31
4 hr.	34.00	0.00816	0.00184	14.65	0.001445	1.27
8 hr.	30.70	0.00736	0.00264	21.86	0.002156	1.22
12 hr.	29.50	0.00708	0.00292	25.23	0.002490	1.17

aaa-Trichloracetophenone

0.001 Mol Ketone + 0.01 Mol KOH

Time	cc. HNO ₃	Mols HNO ₃	Mols Alkali Neutralized	cc. AgNO ₃ 0.0986N	Mols Chlor- ide	Mols Alk. Mols Chloride
5 min.	40.72	0.00980	0.00020	1.23	0.000121	1.65
15 min.	40.16	0.00964	0.00036	2.05	0.000202	1.78
30 min.	39.55	0.00949	0.00051	3.30	0.000225	2.27
1 hr.	37.75	0.00906	0.00094	5.75	0.000567	1.66
2 hr.	36.00	0.00864	0.00136	9.11	0.000898	1.51
4 hr.	32.40	0.00778	0.00222	14.83	0.001463	1.52
8 hr.	28.48	0.00684	0.00316	21.43	0.002113	1.50
12 hr.	26.90	0.00646	0.00354	24.83	0.002450	1.45
24 hr.	24.08	0.00578	0.00422	32.68*	0.00285	1.48

*Normality = 0.0872

aaa-Trichlor-2,4,6-trichloracetophenone

0.001 Mol Ketone + 0.01 Mol KOH

Time	cc. HNO ₃	Mols HNO ₃	Mols Alkali Neutralized	cc. AgNO ₃ 0.0872N	Mols Chlor- ide	Mols Alk. Mols Chloride
5 min.	41.30	0.00991	0.00009	0.60	0.0000524	1.72
15 min.	40.83	0.00980	0.00020	1.57	0.000137	1.46
30 min.	40.16	0.00964	0.00036	3.15	0.000275	1.31
1 hr.	38.90	0.00934	0.00066	5.84	0.000510	1.29
2 hr.	36.94	0.00886	0.00114	10.29	0.000898	1.27
4 hr.	33.85	0.00812	0.00186	16.93	0.001476	1.26
8 hr.	30.75	0.00738	0.00262	24.53	0.00214	1.22
12 hr.	28.93	0.00694	0.00306	28.75	0.00251	1.22

aaa-Trichlor-m-nitroacetophenone

0.001 Mol Ketone + 0.01 Mol KOH

Time	cc. HNO ₃	Mols HNO ₃	Mols Alkali Neutralized	cc. AgNO ₃ 0.0872N	Mols Chlor- ide	Mols Alk. Mols Chloride
5 min.	37.25	0.00894	0.00106	0.70	0.000061	17.4
15 min.	36.83	0.00884	0.00116	1.75	0.000153	7.58
30 min.	36.13	0.00867	0.00133	3.16	0.000276	4.82
1 hr.	35.14	0.00843	0.00157	5.39	0.000470	3.34
2 hr.	33.27	0.00798	0.00202	9.93	0.000866	2.33
4 hr.	30.75	0.00738	0.00262	14.94	0.001303	2.01
8 hr.	27.78	0.00666	0.00334	23.37	0.00204	1.64
12 hr.	25.68	0.00616	0.00384	27.60	0.00241	1.59

aaa-Trichlor-2,4,6-trimethylacetophenone

0.001 Mol Ketone + 0.01 Mol KOH

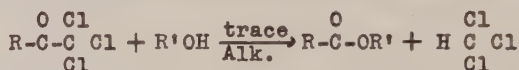
Time	cc. HNO ₃	Mols HNO ₃	Mols Alkali Neutralized	cc. AgNO ₃ 0.0872N	Mols Chlor- ide	Mols Alk. Mols Chloride
5 min.	41.32	0.00992	0.00008			
10 min.	41.20	0.00988	0.00012	0.37	0.0000323	3.72
30 min.	40.64	0.00975	0.00025	1.60	0.000140	1.79
1 hr.	39.42	0.00946	0.00054	4.17	0.000364	1.48
2 hr.	37.37	0.00896	0.00104	8.88	0.000774	1.34
4 hr.	34.18	0.00820	0.00180	16.01	0.001396	1.29
8 hr.	30.96	0.00743	0.00257	23.94	0.00209	1.23
12 hr.	28.84	0.00692	0.00308	28.35	0.002473	1.24

Discussion of Data.--The reaction curves of the *aaa*-trichloracetophenones (with the exception of *aaa*-trichlor-*m*-nitroacetophenone which was known to be impure, see experimental part) closely approximate those of chloroform. In fact the only conclusion that can be drawn from the data is that *aaa*-trichloracetophenones, in dilute alkaline methanol solution, reduce the alkalinity and yield chloride ions at the same rate as chloroform does.

This result is most readily explained in terms of an observation by Houben and Fischer.¹ These workers observed that in addition to the well-known cleavage which takes place in alkaline aqueous solution:



a purely catalytic reaction takes place in alcohols and phenols:



An example given by Houben and Fischer follows. Five grams of *aaa*-trichloracetophenone was dissolved in 15 cc. of methanol and 0.05 grams (0.1 equivalent) of sodium added. Two and eight-tenths grams of methyl benzoate was obtained, constituting a yield of 92% of theory. Basic salts as alkali metal carbonates and acetates were also found effective as catalysts. The reaction proceeds in the presence of as much as 10% water and the reaction is described as being rapid in the cold.

Thus under the conditions which we studied the rates of neutralization of alkali and formation of chloride ions, the primary rapid reaction was:



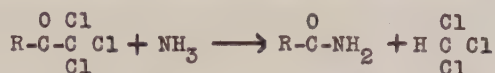
This reaction was of the same order of speed regardless of the presence or absence of substituents ortho to the trichloroacetyl group.

Then in all cases the further slow reaction of chloroform with alcoholic potassium hydroxide was the reaction followed by titration. Since the concentration of chloroform and alkali were

¹J. Houben and W. Fischer, Ber., 64B, 240 (1931); Ber., 64B, 2636 (1931).

the same in all cases, the reaction curves, for neutralization of alkali and formation of chloride ions, were essentially the same.

Ammonolyses.--In connection with the findings of Houben and Fischer, it was of interest to note liquid ammonia caused an analogous reaction to occur. Liquid ammonia dissolves *aaa*-trichloracetophenones and cleaves them according to the equation:



This reaction was found to proceed with *aaa*-trichloracetophenone, *aaa*-trichlor-*m*-nitroacetophenone, *aaa*-trichlor-2, 4, 6-trichloracetophenone, and *aaa*-trichlor-2, 4, 6-trimethylacetophenone. In each case a product was obtained in excellent yield corresponding in properties to the respective acid amides.

Experimental Part

Trichloracetyl Chloride.--Trichloracetyl chloride was prepared according to the method of Delacre.¹ Two hundred and forty-five grams of trichloroacetic acid was heated on the water bath, under reflux, with 140 grams of phosphorus trichloride for two days. The product was purified by distillation, the fraction distilling between 115-117° at atmospheric pressure being retained. A yield of 135 grams of this product was obtained.

aaa-Trichloracetophenone.--Sixty grams of trichloracetyl chloride was slowly added to 22 grams of anhydrous aluminum chloride in 40 grams of benzene and 200 cc. of carbon disulfide. The mixture was refluxed for one-half hour after the addition of the trichloracetyl chloride was complete. The material was then poured upon ice and the carbon disulfide solution separated and dried over calcium chloride. Another preparation was made using 74.5 grams of trichloracetyl chloride, 40 grams of benzene and 27 grams of aluminum chloride in 200 cc. of carbon disulfide. The materials were treated as in the first preparation and the two products combined. After the removal of the carbon disulfide on the water bath, the product was purified by low-pressure distillation. Six fractionations gave 25 grams of pure product distilling sharply at 143° at 26 mm. pressure.

aaa-Trichloracetophenone with ammonia.--About one-half

¹Maurice Delacre, Chemischen Central-Blatt, I, 1197 (1902).

cc. of trichloracetophenone was dropped into about 20 cc. of liquid ammonia. Immediately there appeared on the sides of the vessel, due to splashing, a white crystalline material. The ammonia solution was poured on a watch-glass and evaporated to dryness. A solid was obtained which melted at 124° . After crystallizing from hot water the material melted at 125° . The melting point of the product was not lowered by the addition of Kahlbaum benzamide which melted at 126° .

m-Nitro-acetophenone.--This material was prepared according to the method given in Organic Syntheses¹. Six hundred cc. of concentrated sulfuric acid was placed in a two-liter Erlenmeyer flask surrounded by a heavy ice-salt pack and fitted with a stirrer to provide good agitation. Powdered carbon dioxide was added until the temperature of the sulfuric acid was about -20° . Two hundred and thirty-six Grams of acetophenone was added slowly with addition of carbon dioxide snow to keep the temperature below -10° . After all the acetophenone had been added, the temperature was permitted carefully to rise to 0° to dissolve all the acetophenone. The temperature was then lowered to -10° and a very cold mixture of 160 cc. of concentrated nitric acid and 240 cc. of concentrated sulfuric acid added over a period of thirty minutes using rapid agitation and frequent additions of carbon dioxide snow. When all had been added, the mixture which was a smooth paste, was permitted to rise in temperature to 10° . It immediately was poured into two liters of chipped ice and the whole diluted to four liters with cold water. The pale yellow product thus obtained was separated by filtration, crystallized from 95% alcohol and dried. Two hundred and twelve Grams of the product was obtained, corresponding to a yield of 65% of theory. A repetition of this preparation gave 248 grams of product corresponding to a 75% yield.

m-Nitro-*aaa*-trichloracetophenone (by nitration).--This preparation has been described by Houben². Thirty grams of trichlor acetophenone was dropped into 90 cc. of fuming nitric acid at such a rate that the temperature was maintained at 50° . After

¹"Organic Syntheses," Vol. X, p. 74 (1930): Vol. XI, p. 102 (1931). John Wiley and Sons, Inc., New York City.

²Houben, Ber., 64B, 2651 (1931).

the mixture had stood for one hour it was poured into cold water and the product separated. Houben described the material as an oil, but it was here found to crystallize very readily. After five crystallizations from ligroin, the material still gave high values when analyzed for nitrogen. For this reason the material was purified by low-pressure distillation. At 18 mm. the material distilled between 192-193°. This corresponds to the boiling point as recorded by Houben. The purified product melted but still contained some impurity causing the nitrogen values to be too high. The material was found to contain 5.54% nitrogen. Houben also records a slightly high value of 5.35% nitrogen.

m-Nitro- *aaa*-trichloracetophenone (by chlorination).--

Ten grams of m-nitroacetophenone was melted in a test-tube with a very small amount of anhydrous gold chloride. The temperature was maintained at about 100° and chlorine passed in for six hours, or until the tube had gained nearly the theoretical weight corresponding to the formation of the trichlor derivative. The product was crystallized from ligroin, yielding 9.5 grams or 58% of the theoretical yield. The physical properties corresponded with those of the material obtained by nitrating trichloracetophenone.

m-Nitro- *aaa*-trichloracetophenone with ammonia.--A small

amount of m-nitro-trichloracetophenone was dissolved in a minimum amount of acetone and the solution poured into about 20 cc. of liquid ammonia. After a few minutes the solution was poured on a watch-glass and the volatile liquids permitted to evaporate. The residue, crystallized from water, melted at 142°. Beilstein¹ gives values for the melting point of m-nitro-benzamide ranging from 140-143°.

m-Amino-acetophenone.--Fifty grams of m-nitro-acetophenone was dissolved in 200 cc. of boiling 95% ethyl alcohol in a "Citrate of Magnesia" bottle. About 0.2 grams of Adam's platinum oxide catalyst was added and the bottle placed in a shaking hydrogenator. A pressure of forty to fifty pounds of hydrogen was used and the shaking was continued until the hydrogen pressure did not further drop. The catalyst was removed by filtration and the alcohol removed by distillation. The amine was crystallized from water. From 250 grams of nitro compound there was obtained 184 grams of the amine, corresponding to a yield of 90% of theory.

¹Beilstein, IX, 381.

2,4,6-Tribrom-3-amino-acetophenone.--Fifty grams of m-amino-acetophenone was dissolved in a mixture of 250 cc. of glacial acetic acid and 100 cc. of propionic acid (this mixture was found to remain liquid at low temperatures) and cooled to 0°. One hundred and seventy-eight grams of bromine, dissolved in 250 cc. of glacial acetic acid, was then added slowly to the solution of the amine. The temperature of the mixture was kept below 5° during the entire addition. After all the bromine had been added the solution was permitted to stand one-half hour and then was poured into three liters of ice water. The product was separated by filtration and dried. The 113 grams of crude product obtained corresponded to a yield of 82% of theory. This crude material was used without further purification.

2,4,6-Tribromacetophenone.--Fifty-seven grams of tribrom-aminoacetophenone was dissolved in 500 cc. of boiling alcohol and 25 cc. of concentrated sulfuric acid slowly added. Twenty-one grams of sodium nitrite was added dry to the hot solution as rapidly as the reaction would permit. After all of the nitrate had been added, the solution was allowed to cool and the product precipitated by the addition of water. After separating by filtration, the product was well washed, dried, and distilled under reduced pressure. The fraction distilling between 153-158° at 2 mm. pressure was retained. Forty-seven grams of pure white product so obtained, constituted a yield of 86% of theory and had a melting point of 88°. One crystallization from alcohol raised the melting point to 90°. The melting point recorded by Fuchs¹, after repeated crystallization, was 93.5°.

Chlorination of 2,4,6-tribromacetophenone by sodium hypochlorite solution.--The preparation of *aaa*-trichlor-2,4,6-tribromacetophenone by the action of sodium hypochlorite solution on tribromacetophenone has been described.²

The procedure given follows: "One-half gram of 2,4,6-tribromacetophenone was placed in a flask with 10 cc. of pyridine and 30 cc. of a 10% solution of sodium hypochlorite. After being on the shaker for fifteen hours the flask was removed and the

¹W. Fuchs, Monat. fur Chemie, 36, 136 (1915).

²Reynold C. Fuson, Perry H. Lewis, and Robert N. DuPuis, J. Am. Chem. Soc., 54, 1117 (1932).

small amount of red solid which had separated from the reaction mixture was removed and purified by recrystallization from ligroin. A larger quantity of the product was obtained from the red pyridine layer by acidification and extraction with ether. The product melted at $73-75.3^{\circ}$:"

This procedure was followed carefully three times and no product melting near 73° was obtained. In one experiment the product obtained melted at 72° , but another crystallization raised the melting point to $77-78^{\circ}$, and further work showed it to be identical with the original tribromacetophenone.

Direct chlorination of 2,4,6-tribromacetophenone, $\alpha\alpha\alpha$ -trichlor-2,4,6-tribromacetophenone.--Twenty-five grams of tribromacetophenone was placed in a flask with a small amount of anhydrous gold chloride. The contents of the flask were heated to 200° and chlorine passed in through a fine capillary tube. The temperature of the material was maintained as close to 200° as possible and the chlorination continued for seven hours. At the end of this time the flask and contents had increased in weight two grams. The material was purified by low-pressure distillation, and was obtained as nearly colorless oil. The pure product distilled between 185° and 195° at 25 mm. and between 138° and 140° at about one mm.

Anal:--The analysis was carried out using a Parr Bomb with sodium peroxide, followed by a Volhard titration.

Weight of sample = 0.3243 grams

82.00 cc. of 0.09914 M AgNO_3 solution added.

Back-titrated with 23.13 cc. of KCNS solution

(1 cc. = 0.9951 cc. of AgNO_3 solution)

Found:--0.01834 equivalents of halogen per gram of substance.

Calc. for hexachloracetophenone, $\text{C}_6\text{H}_2\text{OCl}_6$, equivalent of halogen per gram.

$\alpha\alpha\alpha$ -Trichlor-2,4,6-trichloracetophenone with ammonia.--About one-half cc. of the hexachloracetophenone was dissolved in two to three cc. of acetone and the solution poured into 20 cc. of liquid ammonia. After standing for about five minutes the solution was poured on a watch-glass and the volatile liquids permitted to evaporate. The residue on the watch-glass melted at 177° after one crystallization from water. Beilstein(IX, 346),

gives values for the melting point of 2,4,6-trichlorbenzamide as 177° and 181°.

2,4,6-Trimethylacetophenone.--This product was prepared by the method given by Adams and Noller.¹ Seventy-four grams (0.55 mol) of anhydrous aluminum chloride, 150 cc. of carbon disulfide and 30 grams (0.25 mol) of mesitylene were placed in a flask fitted with a reflux condenser and stirring device. Twenty-five and five-tenths grams (0.25 mol) of acetic anhydride was added in fifteen minutes with good agitation. The mixture was refluxed for another thirty minutes by surrounding the flask with a bath of hot water. The contents of the flask were then poured upon ice and the product extracted with ether. After drying the ethereal solution by means of calcium chloride, the ether was removed by slowly dropping the solution into a claisen flask submerged in hot water. The oil remaining in the flask was directly purified by low-pressure distillation. The fraction distilling between 85-90° at 2 mm. pressure was retained. This fraction weighed 36 grams (0.22 mol) and constituted a yield of 89% of theory.

aaa-Trichlor-2,4,6-trimethylacetophenone.--This product was prepared according to the directions of Fuson and Walker.² A solution of 75 grams of sodium hydroxide in 750 cc. of water was chilled and chlorine gas passed in at a fairly rapid rate for fifteen minutes. At this time the solution bleached litmus paper white instantly. Eight grams (8.1 cc.) of the above trimethylacetophenone was added and the mixture stirred vigorously, at room temperature, for seventy hours. After stopping the agitation the oil which settled to the bottom was separated and the aqueous solution extracted with ether. The oil was placed in a small claisen flask submerged in hot water and the ethereal extract slowly dropped in. The oil thus obtained, distilled between 120-150° at about one mm. pressure. Two more runs were made, one using 9.0 grams of the ketone in the above amount of hypochlorite solution and the other using 16.1 grams of the ketone in twice the above amount of solution. The products of the three runs were combined

¹Carl R. Noller with Roger Adams, J. Am. Chem. Soc., **46**, 1892 (1924).

²Reynold C. Fuson and Joseph T. Walker, J. Am. Chem. Soc., **52**, 3274 (1930).

and fractionated three times. The final material was water-white and distilled between 129-132° at 3 mm. pressure. The pure product weighed 32 grams, constituting a yield of 62% of theory. Just before using, the material was re-distilled and the fraction boiling between 144-145° at 7 mm. pressure was retained.

aaa-Trichlor-2,4,6-trimethylacetophenone with ammonia.--

The trichlor-trimethylacetophenone was less soluble in ammonia than the other ketone, hence it was necessary to use more acetone. About one-half cc. of the material was dissolved in 5 cc. of acetone and poured into 20 cc. of liquid ammonia. Since the reaction appeared to be slower in this case than with the other ketones, the mixture was allowed to stand for about one-half hour. The solution was then poured on a watch-glass and the volatile liquids permitted to evaporate. The remaining crystals were placed on a porous plate to remove the adhering oil and washed with petroleum ether. The product melted at 188°. Beilstein (IX, 553), records values for the melting point of 2,4,6-trimethylbenzamide from 187-189°.

Summary

1. The reactions of aaa-trichloracetophenone, aaa-trichlor-m-nitroacetophenone, aaa-trichlor-2,4,6-trichloracetophenone, aaa-trichlor 2,4,6-trimethylacetophenone, and chloroform with dilute alcoholic potassium hydroxide were followed by periodic determination of alkalinity and chloride ion concentration.

2. The neutralization of alkali and the formation of chloride ions in the cases of the aaa-trichloracetophenones and chloroform were found to be essentially the same.

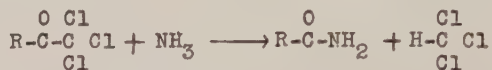
3. The neutralization of alkali and the formation of chloride ions were essentially the same with all the aaa-trichloracetophenones studied regardless of the absence or presence of substituents ortho to the trichloracetyl group.

4. These results were interpreted as follows: The alkali catalyzes the rapid reaction between the aaa-trichloracetophenones and alcohol, giving chloroform and the methyl ester of the respective acid.



The chloroform is then attacked slowly by the alcoholic methanol at essentially the same rate in all cases.

5. Liquid ammonia, at its boiling point, was found to dissolve and react rapidly with *aaa*-trichloracetophenones according to the equation:



6. *aaa*-Trichlor-2,4,6-trichloracetophenone is described as a new compound, and its boiling point recorded.

7. The melting point of *aaa*-trichlor-*m*-nitroacetophenone is recorded for the first time.

